Ground state properties of manganese oxides: Density functional and hybrid density functional calculations

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- Introduction of manganese oxides
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Ground-state properties of multivalent manganese oxides: Density functional and hybrid density functional calculations

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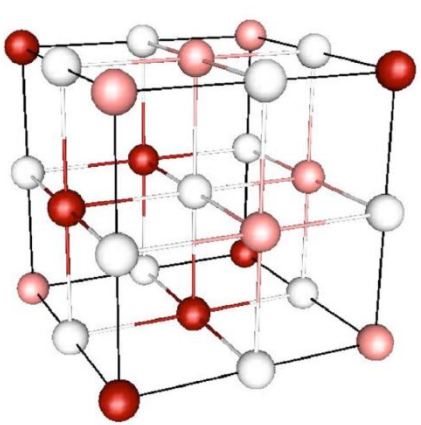
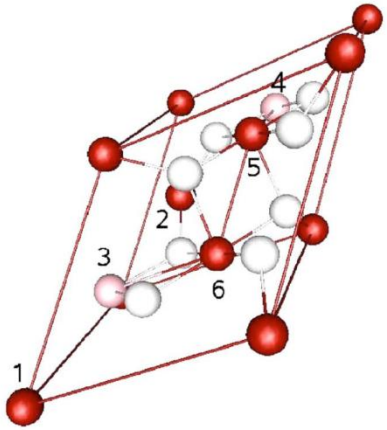
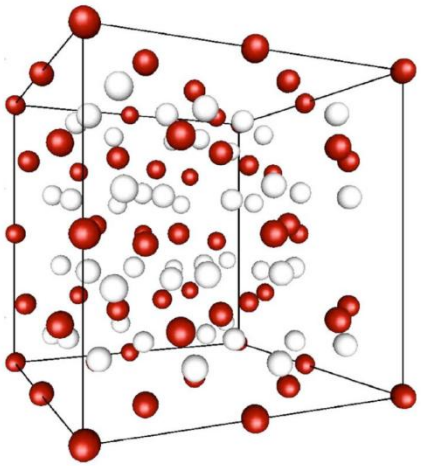
Manganese oxides : experimental results



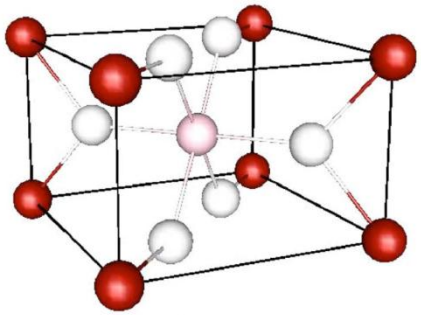
(a)



(b)



(c)



(d)

- (a) MnO : antiferromagnetic insulator and rhombohedrally distorted structure
- (b) Mn_3O_4 :tetragonally distorted spinel structure
- (c) α-Mn_2O_3 :antiferromagnetic transition (80-90K , 25K) and cubic to orthormbic transition (308K) [1968 Grant et al.]
- (d) β-MnO_2 :screw type magnetic structure (below 92K)

Density functional theory

- Vienna ab initio Simulation Package (VASP) program
- 4 methods : PBE, PBE+U (U=6, 4, 3eV), PBE0, HSE
- Standard local density approximation (LDA) or generalized gradient approximation (GGA) : wrong treatment of the Coulomb interaction ➔ limitation in calculation of magnetic materials with strongly localized electronic states

- DFT+U method

- Hybrid functionals : mixture of Hartree-Fock exchange and PBE exchange functional

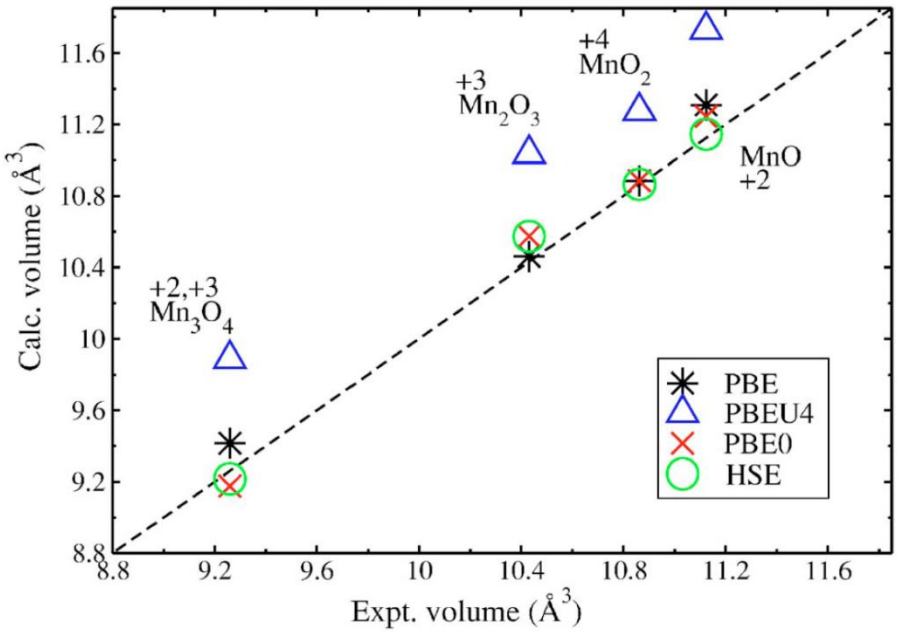
Structural properties

	PBEU6	PBEU4	PBEU3	PBE	PBE0	HSE	Expt.
MnO	45.12	45.10	44.73	43.53	43.54	43.46	43.6[a]
	3.5	3.4	2.6	−0.2	−0.1	−0.3	
Mn_3O_4	166.31	164.20	162.93	158.33	157.42	156.01	155.73[b]
	6.8	5.4	4.6	1.7	1.1	0.2	
α-Mn_2O_3	900.57	882.90	875.65	836.86		845.83	834.48[c]
	7.9	5.8	4.9	0.3		1.4	
β-MnO_2	62.33	59.32	57.82	56.49	55.06	55.30	55.48[d]
	12.5	7.1	4.3	1.8	−0.7	−0.3	
MARE	7.7	5.4	4.1	1.0		0.6	

[a]Ref. 47

- Calculated equilibrium volumes per atom
- relative error
- MARE : average mean absolute relative error

Structural properties



- PBE+U method : significant overestimation of volume
- PBE0, PBE, HSE method : better estimation of volume

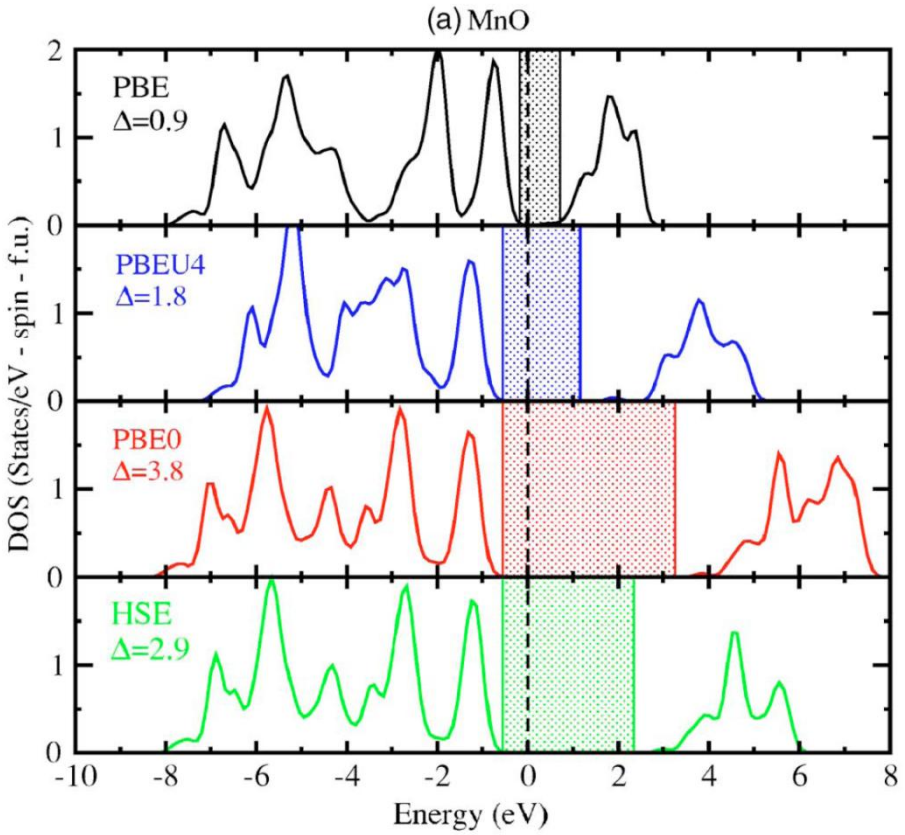
- Generally GGA functionals overestimate the equlibrium volume
- Hybrid functional gives good equilibrium volumes

Magnetic properties

	PBEU6	PBEU4	PBEU3	PBE	PBE0	HSE	Expt.
MnO	AFM-II	AFM-II	AFM-II	AFM-II	AFM-II	AFM-II	AFM-II
	4.67	4.59	4.54	4.31	4.52	4.51	4.58[a]
							4.79[b]
Mn_3O_4	FiM3	FiM3	FiM3	FiM3	FiM3	FiM3	NC-FiM
	3.97–4.67	3.81–4.57	3.72–4.51	3.37–4.22	3.69–4.50	3.68–4.48	
α-Mn_2O_3	FM	FM	FM	AFM	FM	FM	NC-AFM
	4.24	4.07	3.97	2.47–3.72	3.80–3.84	3.81–3.84	3.4–3.9[c]
β-MnO_2	FM	FM	AFM	AFM	AFM	AFM	Helical
	3.34	3.28	2.93	2.51	2.89	2.89	1.84–2.35[c]

- the most stable magnetic configuration and local spin magnetic mement for each structure and applied method
- complicated non-collinear calculation ➔ idealized collinear magnetic couplings (AFM / FM / FiM coupling)
- FiM3=(u u d d u u) , FiM1=(d d u u u u) … FiM6
- PBE0 and HSE

Electronic structure

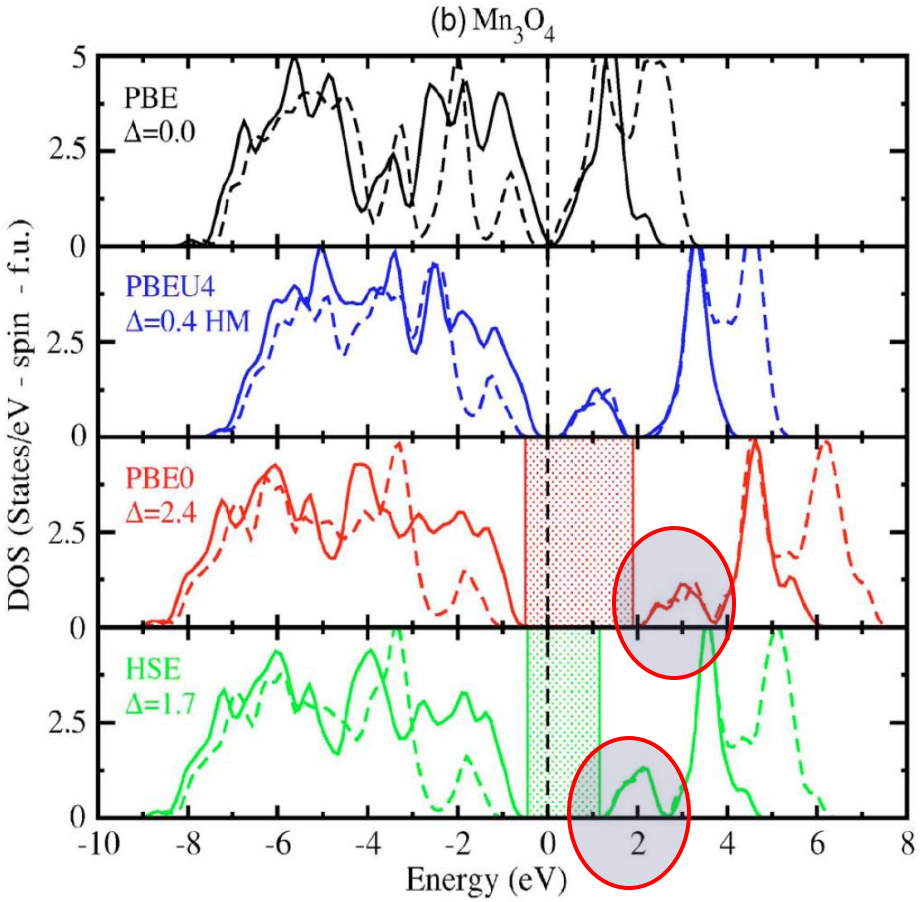


- The total density of states (DOS) for MnO

- The simplest case
- Similar spectrums

- Oxidation state :Mn^{2+} ($3d^5$)
- Five Mn valence electrons fill the majority 3d states

Electronic structure

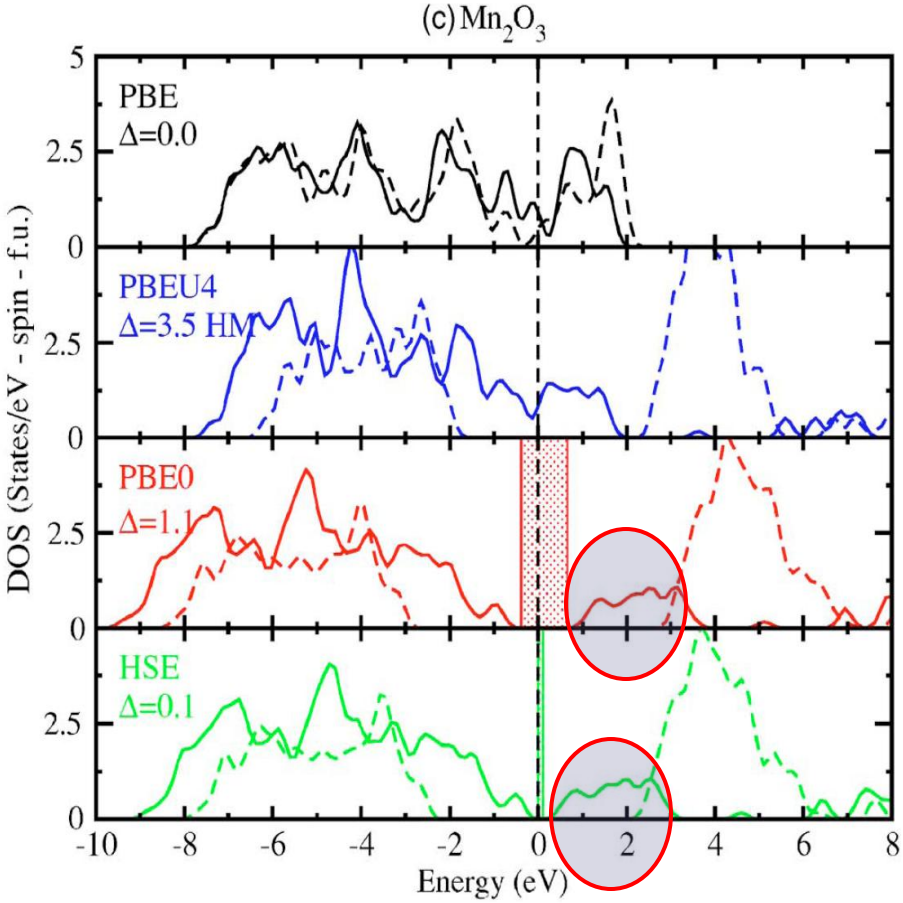


- The total density of states (DOS) for Mn_3O_4
- Hybrid methods make gap

- Mn^{2+} ($3d^5$) in tetrahedral site
  : Five Mn valence electrons fill 3d states
- Mn^{3+} ($3d^4$) in octahedral site
  : Four Mn valence electrons fill 3d states

- Separation of e_g shell one filled and one empty

Electronic structure

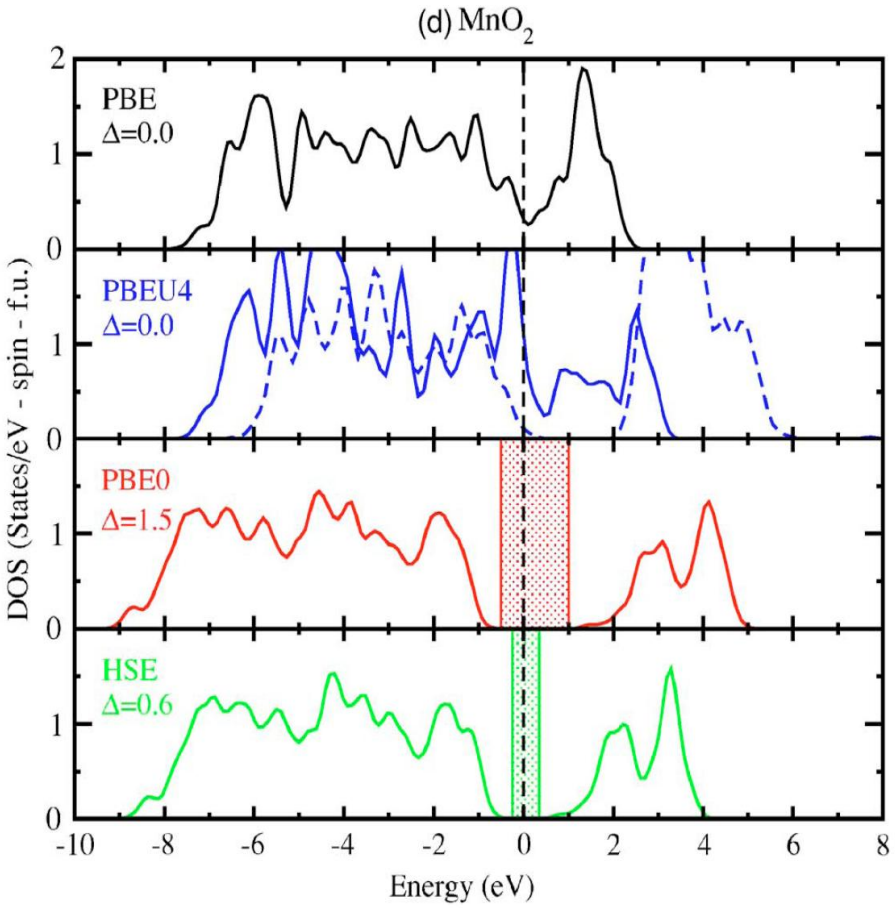


- The total density of states (DOS) for α-Mn_2O_3
- Hybrid methods make gap

- Mn^{3+} ($3d^4$) in octahedral site
  : 4 Mn valence electrons fills 3d state

- Seperation of e_g shell one filled and one empty

Electronic structure



- The total density of states (DOS) for β-MnO_2
- Oxidation state :Mn^{4+} ($3d^3$)
- t_{2g} majority states are occupied and e_g majority states are empty

Conclusions

- PBE0 and HSE yield equilibrium volumes within 1% of the experimental results

- In magnetic properties, PBE+U , PBE0 and HSE is a good method